# THE STRUCTURE OF VINYL COPOLYMERS

## SUPPLEMENT
## THE STRUCTURE OF DIENYNE CYCLIZATION PRODUCTS OF ONE RING

BY
GIFFIN DENISON JONES
B.S., University of Wisconsin, 1939

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL
THE UNIVERSITY OF ILLINOIS, 1942

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## THE STRUCTURE OF VINYL COPOLYMERS

### Introduction

Considerable progress has been made in the study of the structure of vinyl copolymers.[1] A natural extension of this research program was the study of the structure of vinyl copolymers, which have attained great industrial importance. The copolymer selected for this investigation was "Vinylite," prepared by copolymerizing vinyl chloride and vinyl acetate[2].

### Experimental and Discussion of Results

A large number of copolymers of vinyl chloride and vinyl acetate covering the commercially unavailable range of 0 to 50 mol per cent vinyl chloride have been made, purified, and characterized.

Samples of commercial "Vinylites" have been supplemented in study with laboratory-made copolymers of 50 to 100 mol per cent vinyl chloride.

The method of statistical chlorine removal by zinc, previously applied to polyvinyl chloride,[3] has been shown to comply roughly with theory[4] over the whole range of 0 to 100 mol per cent vinyl chloride — this despite complicating factors.

Evidence has been found that the copolymer possesses a head-to-tail orientation of the vinyl chloride and vinyl acetate units. "Vinylite" was hydrolyzed to the polychlorohydrin in aqueous dioxane containing hydrochloric acid; the polychlorohydrin gave a negative test with periodic acid for 1,2-hydroxyls. "Vinylite" liberates no iodine from potassium iodide, indicating the absence of 1,2-chlorines.

The method of interrupted polymerization has been employed to show that, in the copolymerization of a given initial mixture of vinyl acetate and vinyl chloride, the per cent chlorine of the copolymer decreases with increasing per cent yield.

Interrupted polymerizations were made in bulk, in diox-

ane solution, and in emulsion. Agreement was found with the suggestion by Wall[4] that the copolymerization of vinyl chloride and vinyl acetate could be represented by the ratio of unimolecular rate equations; the ratio of the rate constant of vinyl chloride to that of vinyl acetate was in the range 1.5 to 2.0 for room temperature to 60°c. The ratio approached unity as the temperature of copolymerization was increased above 150°c and varied from 10 to 1.5 for copolymerization in methanol containing uranyl nitrate, the high vinyl chloride portion of the polymer precipitating.

Unsuccessful attempts were made to hydrolyze the polychlorohydrin to polyvinyl alcohol. Attempts to convert "Vinylite" to polyvinyl acetate failed also.

## THE STRUCTURE OF DIENYNE CYCLIZATION PRODUCTS OF ONE RING

### Introduction

After previous work[5,6] uncertainty as to the structure of the dienyne cyclization products of one ring concerned the position only of the double bond. This investigation was intended to determine that position.

The dienyne cyclization product 3,4-dimethyl-2,5-diethyl-$\triangle^4$-cyclohexenone or 3,4-dimethyl-2,5-diethyl-$\triangle^2$-cyclohexenone has been prepared from diethyl ketone by the acetylene digrignard method in a yield of 73 per cent based in the dienyne. This is an improvement over the 36 per cent yield reported by Mitchell[6].

A wide variety of conditions has failed to give appreciable yield of the condensation product of the above substituted cyclohexenone with ethyl oxalate.

Alkaline cleavage of the above condensation product gave 0.3 g. of an acid which was ozonized. The isolation of the 2,4-dinitrophenylhydrazone of a ketone believed to be methyl ethyl ketone is an indication that the ethyl oxalate condensation had occured with the unconjugated $\triangle^4$-cyclohexenone.

An attempted condensation of the cyclohexenone with benzaldehyde and sodium methoxide yielded 70 per cent of

recovered cyclohexenone and 20 per cent of impure uncharacterized condensation product.

The cyclohexenone was inert to low pressure hydrogenation with palladium on charcoal. It absorbed between one and two mols of hydrogen at high pressure with Raney nickel and could be re-oxidized with chromic acid.

## References


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## VITA

The writer was born at Fond du Lac, Wisconsin, December 16, 1918. He was reared on a farm, and attended rural school and Fond du Lac High School.

He was graduated from the University of Wisconsin in June, 1939, with the degree of B.S. in Chemistry.

For the year 1939-40 the writer was a teaching assistant in organic chemistry at the University of Illinois. Two university fellowships were granted him from 1940 to 1942.

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